(54) Title: PROCESS BASED ON THE USE OF ZEOLITES FOR THE TREATMENT OF CONTAMINATED WATER

TCE/silicalite - Langmuir isotherm
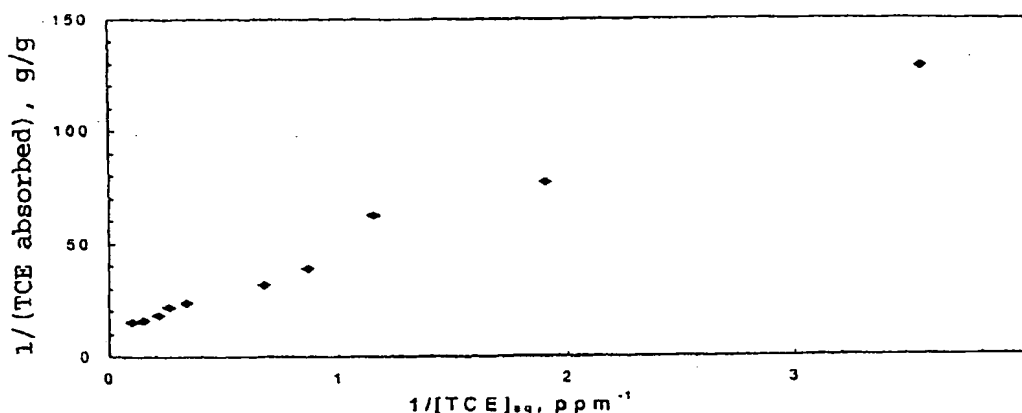
Langmuir isotherm for the adsorption of TCE on Silicalite

(57) Abstract: A process is described for the treatment of water contaminated by apolar compounds consisting of halogenated solvents, aliphatic compounds, aromatic compounds or their mixtures which consists in treating the water with one or more apolar zeolites characterized by a silica/alumina ratio > 50 and by the presence of structural channels having dimensions similar to those of the molecules of the contaminating compounds.

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— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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PROCESS BASED ON THE USE OF ZEOLITES FOR THE TREATMENT OF CONTAMINATED WATER.

The present invention relates to a process for the

10   treatment of water contaminated by apolar compounds based on the use of particular zeolites.

, More specifically, the invention relates to a process for the treatment of water contaminated by apolar compounds consisting of halogenated organic solvents and aromatic hy-

15   drocarbons which is based on the use of apolar zeolites having structural channels with specific dimensions.

The process according to the invention can be conveniently used for the treatment of contaminated groundwater by the use of a permeable reactive barrier (PRB).

20   Conventional PRB for the decontamination of water contaminated by halogenated solvents are based on systems using metallic iron and/or granulated activated carbon (GAC).

The first system, functioning for the reducing capacities of the metal, is only active towards reducible sub-

25   stances, such as organo-chlorinated products or metals with

a high oxidation number (US 5,266,213, WO 92/19556).

Furthermore, when zero-valent iron is used, there is a reduction in the permeability of the barrier due to encrustations or the precipitation of minerals which derive from

5   the reactions between the ions of the oxidized metal and the substances contained in the groundwater.

The second system is a non-specific absorbent and as such is not very selective with respect to interfering substances present in the water and in particular in groundwa-

10   ter (ions, humic acids, etc.).

If it is used for the production of permeable reactive barriers, it consequently causes exhaustion of the system in short times (Williamson, D. 2000. Construction of a funnel-and-gate treatment system for pesticide-contaminated

15   groundwater. Chemical Oxidation and reactive barriers. Godage B. et al. Eds. In II Intl. Conf. on Remediation of chlorinated and recalcitrant compounds. Monterey, CA, USA, Battelle Press, Columbus, (2000)), pages 257-264.

Schad, H 2000. Funnel-and-gate at a former manufac-

20   tured gas plant site in Kalsruhe, Germany: design and construction. In: Chemical Oxidation and reactive barriers. Godage B. et al. Eds., II Intl. Conf. on Remediation of chlorinated and recalcitrant compounds. Monterey, CA, USA, Battelle Press, Columbus, (2000), 215-322.

25   Both systems however prove to be ineffective in remov-

ing all the main pollutants often contemporaneously present in contaminated groundwater beneath industrial sites, which frequently consist of apolar compounds such as halogenated solvents and compounds deriving from the oil industry.

5   These are often highly toxic products, some of which are of a carcinogen nature, whose concentration in underground water must respect the strict limits established by the law.

A treatment process of contaminated water has now been found, which allows the above pollutants to be effectively

10   and selectively removed with respect to the mineral salts normally dissolved in water.

An object of the present invention therefore relates to a process for the treatment of water contaminated by apolar compounds which consists in treating the water with

15   one or more apolar zeolites characterized by a silica-alumina ratio > 50 and by the presence of structural channels having dimensions similar to those of the molecules of the contaminating compounds.

The process according to the invention is particularly

20   effective in removing pollutants consisting of halogenated solvents such as carbon tetrachloride, tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), vinylchloride (VC) and aliphatic and/or aromatic compounds deriving from the oil industry such as methyl-terbutylether

25   (MTBE), BTEX (benzene, toluene, ethylbenzene, xylenes),

naphthalene, 2-methyl-naphthalene, acenaphthene, phenan-threne.

The process according to the invention can be conveniently used for the decontamination of groundwater by the

5   use of permeable reactive barriers (PRB). In this case, the zeolite forms the active medium of the barrier, placed in situ perpendicular to the flow of the groundwater, which when crossed by the polluted water column allows decontamination by the immobilization of the contaminating species.

10   The barriers can treat groundwater polluted by chlorinated solvents, cyclic or polycyclic aromatic hydrocarbons and compounds which are particularly resistant both to biodegradation and adsorption such as MTBE or vinyl chloride (VC), with a high selectivity with respect to inor-

15   ganic interfering products.

Vinyl chloride is considered as being a contaminant which is difficult to eliminate. It is not sufficiently withheld, in fact, by activated carbon and its degradation requires the use of additional structures which involve the

20   use of UV lamps.

The presence of MTBE in groundwater also represents a problem which is difficult to overcome and whose solution justifies the use of relatively costly absorbing materials (Davis et al., J. Env. Eng., 126, page 354, April 2000).

25   The zeolites used in the process of the invention are

characterized by the presence of structural channels having

dimensions ranging from 4.5 to 7.5 Å. Zeolites having

structural channels with dimensions ranging from 5 to 7 Å

and silica/alumina ratios > 200 such as, for example, sili-

5   calite, ZSM-5 zeolite, mordenite, are preferably used.

As a result of their selectivity, zeolites have a

higher absorption capacity and functioning duration than

those of materials currently used in permeable reactive

barriers, such as activated carbon.

10   This is due to the properties of this reactive medium

which are based on the dimension of the structural chan-

nels, suitably calibrated for organic molecules, and on the

high apolarity, deriving from high silica/alumina ratios,

which excludes any type of interaction with ions or polar

15   compounds.

The zeolite therefore has a selective interaction with

molecules of apolar contaminants whereas it completely ex-

cludes polar ions and molecules normally present in ground-

water together with humic substances, having higher molecu-

20   lar dimensions than those of the structural channels.

Suitable mixtures of particular zeolites, moreover,

allow the contemporaneous removal of aliphatic organo-

chlorinated products, aromatic hydrocarbons, polyaromatic

hydrocarbons, characteristic components of oil products.

25   ZSM-5 zeolite and mordenite, with an Si/Al ratio >

200, are materials known as molecular sieves or as carriers for catalysts, but their use as active components for the production of PRB has not yet been described in literature.

ZSM-5 zeolite is particularly suitable for aliphatic,
5   halogen-aliphatic and mono-aromatic molecules, such as BTEX and halogen-benzene-derivatives.

Mordenite, on the other hand, is suitable for aromatic molecules with two or more aromatic rings, and halogen- and alkyl-substituted.

10 <u>Description of the methods used for measuring the proper-ties of the active materials</u>

<u>General procedure</u>

The materials, in a quantity of 10 mg, unless other-wise indicated, are incubated in 20 ml of water in a tube
15 with a Teflon plug closed with a metal collar with a mini-mum headspace to allow stirring; the contaminating com-pound (up to 100 µl of an aqueous solution at a suitable concentration) is added with a 100 µl syringe; the stirring is carried out in a complete rotation system (powder
20 mixer). At the end of the reaction, after 24 hours, at much higher times, therefore, than the equilibrium times deter-mined for each adsorbent, the mixture is centrifuged for 15' at 700 rpm to separate the adsorbing material and the non-adsorbed contaminant is determined from its residual
25 concentration in solution. Each determination is carried

out at least three times. For each determination the sample
and control consisting of liquid and contaminant without
adsorbing material are prepared under the same conditions.
This procedure is followed for all the contaminants exam-

5   ined.

Determination of the equilibrium times

From 10 mg to 1 g of adsorbing material are left to
incubate with 20 ml of water containing from 100 ppb to 5
ppm of contaminant under stirring at room temperature for

10   times varying from 15' to 48 h. The equilibrium time is
considered as being that over which the adsorption has not
increased. In studying the effects of the conditions on the
adsorption, the quantity of adsorbing material is used
which determines the adsorption of at least half of the

15   contaminant put in contact therewith.

Analysis of TCE, PCE, VC, TOLUENE, MTBE, Naphthalene, 2-
methyl-naphthalene, acenaphthene, phenanthrene (solution)

The aqueous solution is extracted with hexane in the
ratio 5.666/1 (H_2O/hexane), in a tube analogous to the re-

20   action tube; a millilitre of hexane is removed for analysis
in GC-ECD, or GC-FID. The control consists of the sample,
without the adsorbing material, subjected to the same
treatment.

GC/MS analysis of TOLUENE/MTBE in a mixture

25   The analysis is carried out from suitable aqueous so-

lutions, measuring the contaminants in the headspace. The system used was GC/MS/DS Mod. MAT/90 of Finnigan; the gaschromatographic column used was a PONA (length 50 m x 0.21 I.D. and 0.5 µm of film) of Hewlett-Packard. The flow

5 of the carrier measured at 35°C proved to be 0.6 ml/min (Helium). 500 µl of the headspace of each sample were injected, removing them with a (heated) gas syringe, from the phial kept for 2 h at 70°C to reach equilibrium. The mass spectrometer operated in E.I. (electronic impact) at 70 eV

10 and at a resolution of 1500 within the mass range of 30-120 a.m.u. and at a scanning rate which was such as to acquire a spectrum every 0.8 s.

Effect of the ionic strength and pH on the adsorption

The adsorption is carried out at different concentra-
15 tions of $CaCl_2$: 5-100 mM; for the pH, solutions were tested at pH 6, 7, 8 obtained with an Na Phosphate 20 mM buffer.

Adsorption reaction with real groundwater

The groundwater of a contaminated site was used. The chemical composition for the inorganic components tested us
20 as follows:

Cations (mg/l)

Iron: 8.6; Nickel: 0.05; Manganese: 1.7; Lead: < 0.01; Zinc: < 0.8.

Sodium: 371; Potassium: 12; Magnesium: 60; Calcium: 298;
25 Anions (mg/l)

Carbonates: 475; Chlorides: 2300; Nitrates 13; Nitrites 3;

Sulfates 14000.

EXAMPLE 1

Table 1 indicates the adsorption data obtained with

5   TCE with different adsorbing materials.

Table 1. Adsorption of TCE with GAC and zeolites

Contaminant: 300 ppb of TCE; Conditions: contact time 1 h

Adsorbent	Quantity (mg)	Quantity adsorbed (% of initial amount)
GAC	10.8	55
Silicalite	11.1	94
ZSM-5	13.3	97
β-zeolite	11.4	33

The zeolites examined, silicalite and ZSM-5, gave bet-

15 ter performances, much higher than those of GAC. β-zeolite,

although characterized by structural channels of 7.5 Å with

slightly larger dimensions than those of silicalite and

ZSM-5, both with channels of 5 Å, has a silica/aluminum ra-

tio of 70 and therefore lower than both that of ZSM-5, 290,

20 and that of silicalite, infinite.

These ratio values, indicating a higher polarity of β-

zeolite, are, together with the different structural chan-

nel dimensions, responsible for its different behaviour.

EXAMPLE 2

25 The adsorption kinetics were also determined for sili-

calite, by measuring the quantity of TCE adsorbed at various times. The following conditions were used in the example:

The adsorbing material, 10 mg, was incubated in 20 ml
5   of water for 1 h in a 20 ml tube with a Teflon plug closed with a metallic collar with a minimum headspace to allow stirring; TCE, about 100 µl of an aqueous solution at a suitable concentration, to give an initial concentration of 300 ppb to the solution to be subjected to absorption, was
10   subsequently added; the stirring was carried out in a mixer.

At the end of the reaction, 2 ml of aqueous phase are removed with a syringe and centrifuged in an Eppendorf phial at 15000 rpm for 5' to separate the silicalite from
15   the TCE solution.

TCE analysis (solution): the aqueous solution (1 ml) is extracted with hexane (0.5 ml); 100 µl of the extract are removed for analysis in GC-ECD. The control consists of the sample, without the adsorbing material, subjected to
20   the same treatment.

The data at different times are indicated in Table 2.

25

Table 2: adsorption kinetics of TCE/Silicalite

Quantity of silicalite (mg)	Time (minutes)	TCE Adsorbed (%)
10.8	5	76
10.1	10	81
10.3	15	90
10.5	30	92
11.3	45	93
10.0	60	93

These dosages seem to indicate very short adsorption times, in the order of 10 minutes or less.

EXAMPLE 3

The adsorption isotherm of trichloroethylene on silicalite was obtained from adsorption experiments with initial concentrations within the range of 50 ppb - 100 ppm. Figures 3 and 4 below indicate the results obtained; each point is the average of three determinations. The linearity of the curve of figure 1, represented according to the Langmuir method, shows the good correspondence of the data with the Langmuir isotherm (Figure 1).

The adsorption efficiency under the experimental con-

ditions (10 mg of adsorbing material in 20 ml of water, contaminating at different concentrations) is indicated in figure 2.

EXAMPLE 4

5   Various adsorption experiments were carried out in the presence of strong concentrations of salts.

No significant effect of the ionic strength on the adsorption of TCE was observed (figure 3).

EXAMPLE 5

10   Adsorption on Silicalite of TCE in real groundwater.

The influence of the cations and anions normally present in groundwater was examined using, in the reaction, real polluted groundwater whose content of sulfates was much higher than 10 g/l. 100 pmm of TCE were added, to 20

15   ml of groundwater in the laboratory reaction. After incubation with 10 mg of silicalite, the water was analyzed and the quantity of TCE removed from the water proved to be higher than 95%, very clearly demonstrating the adsorption selectivity of the silicalite.

20   EXAMPLE 6

Adsorption of PCE

The experimental conditions were the same as those of TCE.

25

Table 3. Adsorption of PCE with silicalite

Quantity of Silicalite (mg)	initial [PCE] (ppb)	[PCE] adsorbed (% initial)
11.4	250	94
11.4	500	96
11.8	750	96
12.0	1000	97

EXAMPLE 7

In order to demonstrate the competitive effects of the two compounds TCE and PCE, adsorption tests were effected with a mixture containing both. The results, indicated in Table 4 below, show the absence of inhibition of one contaminant with respect to the other. On increasing the concentration of PCE, in fact, from 250 to 1000 ppb, the adsorption of TCE was not substantially modified.

Table 4. Adsorption of mixtures of PCE and TCE

Quantity silicalite (mg)	Quantity TCE (ppb)	Quantity PCE (ppb)	TCE adsorbed (%)	PCE adsorbed (%)
12.0	1000	250	93	93
11.8	1000	500	93	95
10.8	1000	750	94	96
10.6	1000	1000	95	96

EXAMPLE 8

Adsorption of Vinyl chloride (VC)

An examination of aliphatic organo-chlorinated compounds cannot exclude VC which is the most difficult compound to degrade in this group.

Figure 4 below indicates the Freundlich isotherm obtained in the treatment of VC on silicalite; conditions: 10 mg of adsorbing material, contaminant between 550 and 5550 ppb, in 20 ml of water.

EXAMPLE 9

In this example, the adsorption capacities of zeolites and GAC were compared.

The results obtained, under analogous conditions to the previous ones, are indicated in Table 5.

Table 5. Adsorption of VC with silicalite, ZSM-5 and GAC

Type of Adsorbent	Quantity of Adsorbent (mg)	initial VC (ppb)	VC Adsorbed (%)
Silicalite	10	555	94
Silicalite	10	1105	92
Silicalite	10	1660	93
Silicalite	10	5550	94
ZSM-5	10	5550	99
GAC	10	555	45

EXAMPLE 10

Adsorption of toluene

Toluene is considered as being the most representative BTEX compound present in fuels, and as such is normally the reference chemical compound of aromatic hydrocarbons. The results obtained at concentrations normally found in contaminated groundwater are indicated in figure 5.

A comparison between zeolites differing in the adsorption of toluene is provided in Table 6 below.

Table 6. Comparison between zeolites differing in the adsorption of toluene.

Type of zeolite	Quantity in the test (mg)	[Toluene] initial (ppm)	Toluene adsorbed (%)
Silicalite	10.3	50	75
ZSM-5	10.2	50	85
β-zeolite	10.2	50	15

The results showed that ZSM-5 and silicalite have a comparable behaviour.

<u>EXAMPLE 11</u>

In the comparison between silicalite, ZSM-5 and GAC, for the adsorption of contaminated mixtures, organochlorinated and aromatic hydrocarbons, the results indicated in the following table were obtained.

Table 7. Comparison between silicalite, ZSM-5 and GAC in the adsorption of Toluene + PCE + TCE mixtures

Conditions: the same as the previous examples, 20 ml of water containing the contaminants at the concentrations indicated, contact times higher than the equilibrium time.

...

Table 7. Comparison between silicalite, ZSM-5 and GAC in the adsorption of Toluene + PCE + TCE mixtures

Type Adsorbent	Toluene	PCE	TCE	Toluene	PCE	TCE
	Initial concentration (ppb)			Quantity adsorbed (%)		
Silicalite	5000	1000	1000	93	92	95
ZSM-5	5000	1000	1000	98	98	99
GAC	5000	1000	1000	78	48	52

The results indicate the absence of inhibition between the different molecules with respect to the absorption sites of the zeolite.

EXAMPLE 12

Both silicalite and ZSM-5 seem to be also effective in the adsorption of MTBE, a compound which is difficult to biodegrade and difficult to treat with activated carbon. The comparison is provided in Table 8.

Table 8. Comparison between silicalite and ZSM-5 in the adsorption of MTBE

Type of zeolite	Quantity (mg)	initial [MTBE] (ppb)	[MTBE] absorbed (%)
Silicalite	10.4	1000	96
ZSM-5	10.2	1000	98

EXAMPLE 13

The study of MTBE was further developed with respect

to GAC, with different contact times: with silicalite it
was 1 h, for carbon 4 h. The results are indicated below.

Table 9. Comparison between activated carbon and silicalite
for the adsorption of MTBE

Type of ad-sorbent	Quantity of adsorbent (mg)	initial [MTBE] (ppb)	MTBE adsorbed (%)
Silicalite	10.1	1000	97
Silicalite	10.2	5000	96
Silicalite	10.0	20000	90
GAC	10.3	1000	80
GAC	10.1	20000	51
GAC	50.4	1000	88
GAC	50.2	20000	90

As shown by the results, the comparison is in favour of the
silicalite.

EXAMPLE 14

Mixtures of Toluene/MTBE were tested with silicalite
to show any possible reciprocal inhibitions; the comparison
of silicalite with GAC was then effected on these mixtures
of contaminants.

Table 10. Adsorption of mixtures of Toluene/MTBE:
GAC/Silicalite comparison

Type of ad-sorbent	Quantity adsorbent (mg)	initial MTB (ppb)	initial Toluene (ppb)	MTBE adsorbed (%)	Toluene adsorbed (%)
Silicalite	11.2	1000	5000	97	95
GAC	11.2	1000	5000	69	82
	51.5	1000	5000	82	83

In conclusion, the adsorbing capacities of silicalite were
demonstrated, which proved to be very similar to those
shown by the commercial product ZSM-5. The fact that these
adsorbents have better adsorption characteristics than GAC
was confirmed.

EXAMPLE 15

Polycyclic aromatic hydrocarbons

Naphthalene was examined as aromatic compound with two
condensed rings and adsorption experiments were effected
with Silicalite, ZSM-5, MSA, ERS-8, Mordenite, GAC.
Conditions: equilibrium time 24 h, 10 mg of adsorbent, 1
ppm of naphthalene, in 22 ml of water.

Table 11. Adsorption of Naphthalene with different adsorb-
ents.

Type of adsorbent	Quantity of adsorbent (mg)	Initial Naphthalene (ppb)	Naphthalene adsorbed (%)
Silicalite	10.2	1000	18
ZSM-5	10.3	1000	33
MSA	10.5	1000	5
ERS-8	10.2	1000	5
Mordenite	10.5	1000	100
GAC	11.2	1000	72
GAC	50.5	1000	81

EXAMPLE 16

Molecules of components of gas oil were also examined,
in particular 2-methylnaphthalene, acenaphthene and phenan-
threne; the results obtained with Mordenite and with MSA
under the conditions of 10 mg of adsorbent in 22 ml of wa-
ter containing 1 ppm of contaminant are indicated in Table
12 below.

Table 12. Adsorption of polycyclic aromatic hydrocarbons with mordenite and MSA

Type of adsorbent	initial 2-methyl-Naphthalene (ppb)	initial Acenaph-thene (ppb)	initial Phenan-threne (ppb)	2-methyl-Naphtha-lene adsorbed (%)	Acenaph-thene Adsorbed (%)	Phenan-threne Adsorbed (%)
Mordenite	1000	1000	1000	100	95	100
MSA	1000	1000	1000	15	5	22

EXAMPLE 17

Comparison between a metallic iron barrier and a zeolite barrier.

Figure 6 shows the chain of transformations undergone by tetrachloroethylene, at a concentration of 1 ppm, in groundwater which moves at a Darcy velocity of 1 m/day, in a reactive barrier containing granular Fe°. The kinetics were calculated from the data of Tratnyek et al. (P.G.Tratnyek, T.L. Johnson, M.M. Scherer, G.R. Eykholt, GWMR, Fall 1997, pages 108-114), assuming that the Fe° has a reactive surface of 3.5 m^2/cm^3, i.e. among the highest specified in literature. The concentration trend of the decay products is indicated, in relation to the run in the barrier: tetrachloroethylene (PCE) → trichloroethylene (TCE) → dichloroethylene (DCE) + acetylene and chloroace-

tylene (AC); dichloroethylene → vinyl chloride (VC) →

ethylene. The chloroacetylene degrades rapidly into acety-

lene and vinyl chloride (Figure 6).

PCE is rapidly decomposed, but the further reaction of

5   its decay products is slower, requiring about two days

residence, corresponding to a run of a few metres in the

barrier, to obtain the degradation of the last dangerous

species of the chain, vinyl chloride. This makes it neces-

sary to have a barrier thickness, under these conditions,

10   of at least 3-5 metres.

For iron barriers, the well-known limits, amply indi-

cated in literature, should be pointed out, according to

which the efficacy is acknowledged only for a few groups of

reducible products, aliphatic chlorinated products and

15   heavy metals with a high oxidation number, for example

Cr^{+6}, U^{+6}; the functioning dependence on the presence of

ions which considerably reduce the performances, is also

fully described (Dahmke, A., E. Ebert, R. Kober and D.

Schafer. 2000. Laboratory and field results of Fe(0) reac-

20   tion walls - a first resumè. In: Proc. Intl. Conf. Ground-

water Research, Rosbijerg et al. Eds. Copenhagen (2000),

page 395-396.

EXAMPLE 18

Functioning of a zeolite barrier.

25   Zeolites, even with relatively large particles sizes,

- 22 -

thanks to their microporous structure, allow a much more rapid adsorption, with times which can easily be in the order of a second and, consequently, in a run of fraction of cm in a barrier.

5 The thickness of a zeolite absorbing barrier does not therefore depend on the kinetics, but only on the absorbing capacity of the zeolite itself with respect to the species to be adsorbed.

 Figure 7 shows the simulation, based on the adsorption isotherm data, measured on the materials used in the proc-

10 ess, object of the present invention, of the functioning of a zeolite barrier after a year; the groundwater, which moves at 1 metre/day, has a pollution of 1 ppm of trichloroethylene (TCE). After 1 year, the first layers of the

15 barrier, for a thickness of about 1 cm, are therefore saturated, having adsorbed the whole quantity of TCE corresponding to their capacity, on the basis of the isotherm. Correspondingly, the TCE passes with an unaltered concentration. Downstream of this layer, the concentration drops

20 extremely rapidly (Figure 7).

 Figure 8, again calculated with the data of the materials used in the process, object of the invention, shows, on the other hand, the advance of the saturation front in the time calculated, in a zeolite barrier, under various

25 conditions of groundwater concentrations and velocity (Fig-

ure 8).

This graph can therefore be used for estimating the thickness required for maintaining the barrier effective for a certain period of time, assuming that the groundwater
5 only contains TCE. If other organic molecules are present, the thicknesses necessary for absorbing these other molecules must be naturally added to that obtained from figure 8.

One of the strong points of zeolites is that they do
10 not have adsorption inhibition, of one organic molecule on the part of another and, above all, that there is no competition for the adsorption sites on the part of ions up to high concentrations. This is particularly important as, if the material also absorbed ions, it would very rapidly be-
15 come exhausted as the ions are often hundreds or thousands of times more numerous than the organic molecules.

20

25

CLAIMS

1. A process for the treatment of water contaminated by apolar compounds which consists in treating the water with one or more apolar zeolites characterized by a silica/alumina ratio > 50 and by the presence of structural channels having dimensions similar to those of the molecules of the contaminating compounds.

2. The process according to claim 1, wherein the apolar compounds consist of halogenated solvents, aliphatic compounds, aromatic compounds or their mixtures.

3. The process according to claim 1, wherein the zeolite is characterized by the presence of structural channels having dimensions ranging from 4.5 to 7.5 Å.

4. The process according to claim 3, wherein the zeolite is characterized by the presence of structural channels having dimensions ranging from 5.0 to 7.0 Å.

5. The process according to claim 1, wherein the zeolite is characterized by a silica/alumina ratio > 200.

6. The process according to claim 5, wherein the zeolite consists of silicalite or ZSM-5 zeolite.

7. The process according to claim 1, wherein the treatment is effected on contaminated groundwater and consists in passing the water through a permeable reactive barrier (PRB), placed in situ perpendicular to the flow of the groundwater, whose reactive medium

consists of zeolite.

8.   The process according to claim 2, wherein the halogen-
     ated solvents consist of carbon tetrachloride, tetra-
     chloroethylene (PCE), trichloroethylene (TCE), dichlo-
5   roethylene (DCE), vinylchloride (VC), the aliphatic
     and aromatic compounds consist of methyl-terbutylether
     (MTBE), BTEX (benzene, toluene, ethylbenzene, xy-
     lenes), naphthalene, 2-methyl-naphthalene, acenaph-
     thene, phenanthrene.

10 9.   The process according to claim 1, wherein the water is
     treated with a mixture of zeolites defined in claim 1,
     in relation to the type of contaminants present in the
     water itself.

10. The process according to claim 1, wherein the water is
15   contaminated by aliphatic, halogen-aliphatic and mono-
     aromatic apolar compounds, such as BTEX and halogen-
     benzene-derivatives and ZSM-5 zeolite.

11. The process according to claim 1, wherein the water is
     contaminated by aromatic compounds with two or more
20   aromatic rings, halogen- and alkyl-substituted and the
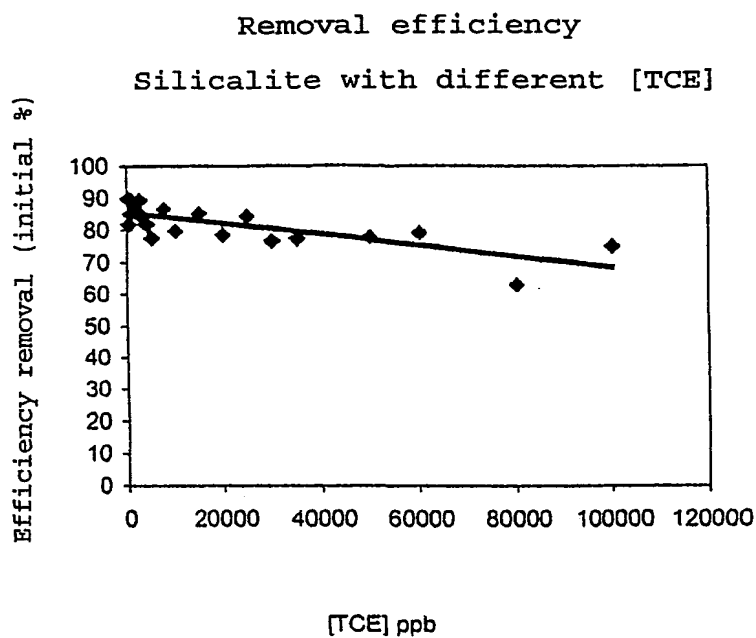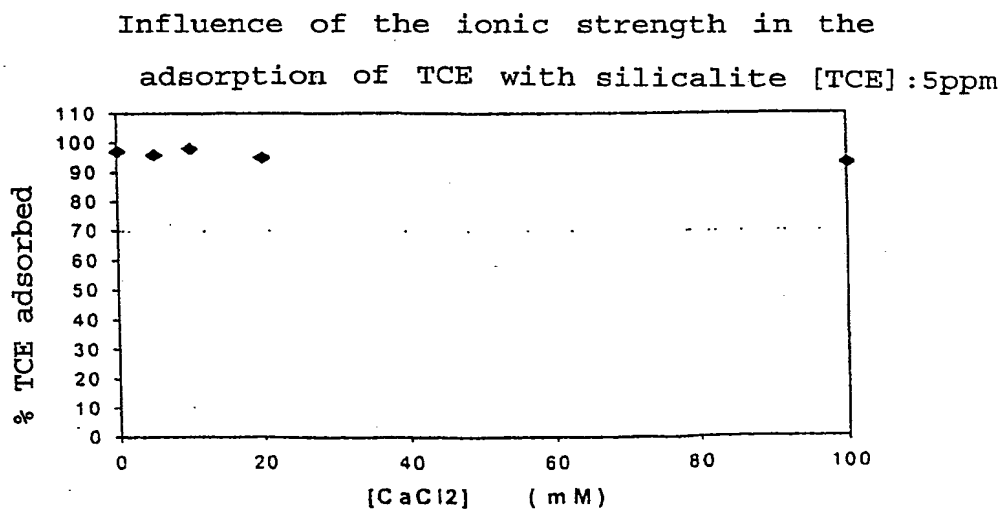   zeolite is mordenite.

25

TCE/silicalite - Langmuir isotherm

Langmuir isotherm for the adsorption of TCE on Silicalite
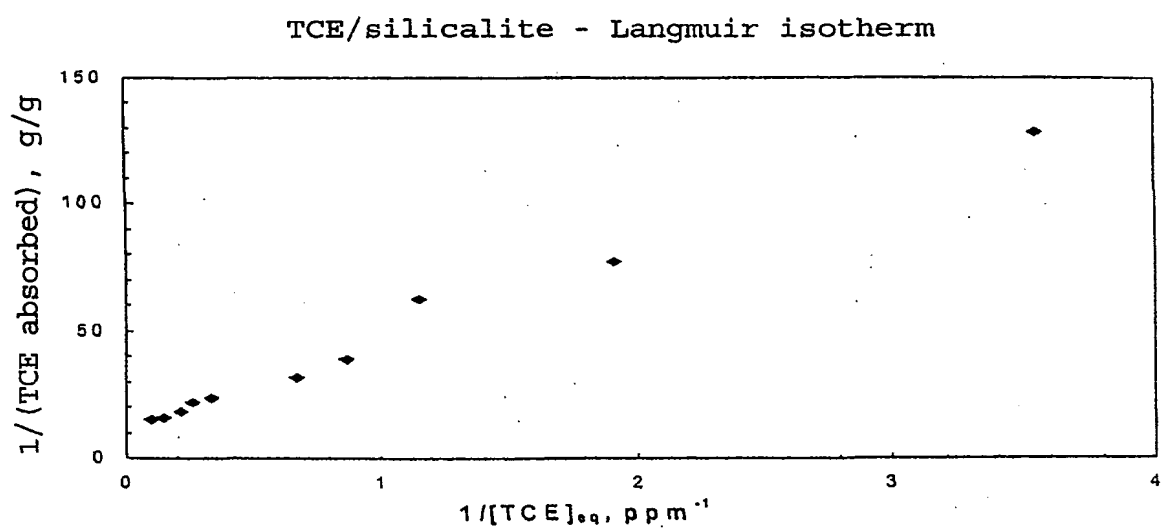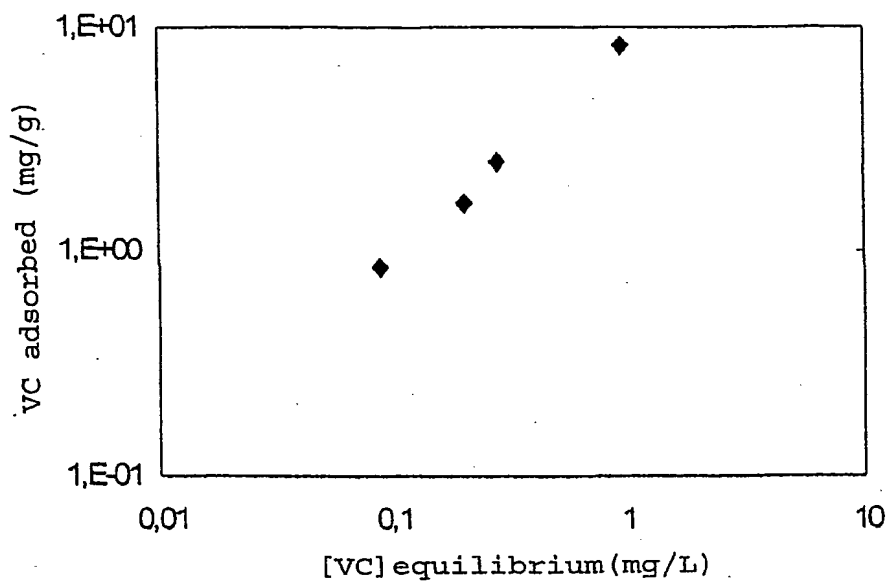
Fig.1

Removal efficiency

Silicalite with different [TCE]

Fig.2   Removal efficiency of TCE from different solutions with silicalite

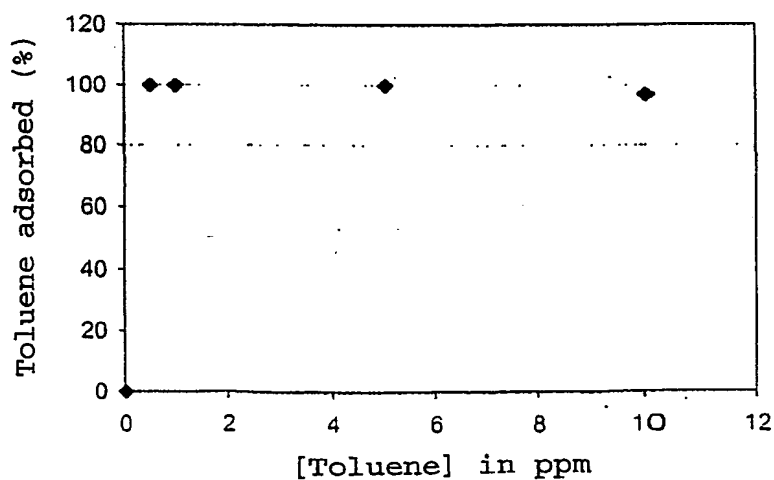Influence of the ionic strength in the adsorption of TCE with silicalite [TCE]:5ppm

Fig.3   Influence of the ionic strength

Freundlich isotherm VC adsorption/Silicalite
(log/log)

Fig.4   Freundlich isotherm for the adsorption of
VC on silicalite

**Fig.5**   Adsorption of Toluene on Silicalite
(average concentrations observed in the
groundwater)

PCE and its decay products in an Fe° barrier
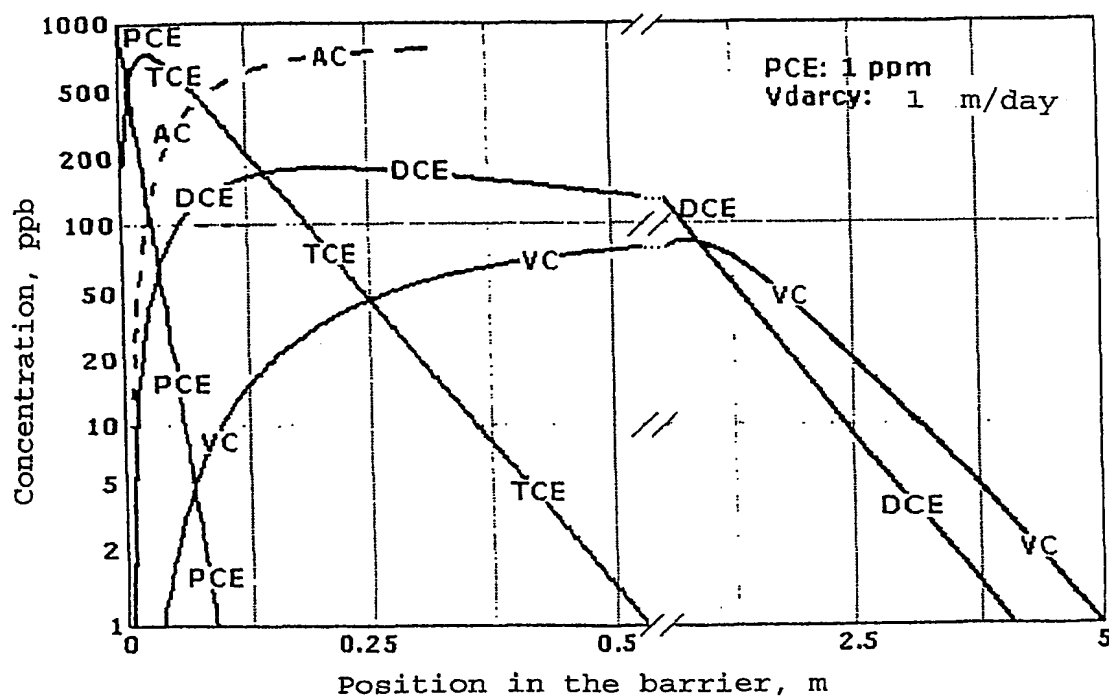
Transformations undergone by tetrachloroethylene, at a con-
centration of 1 ppm, in groundwater which moves at a Darcy
velocity of 1 m/day, in a reactive barrier containing
granular Fe°.

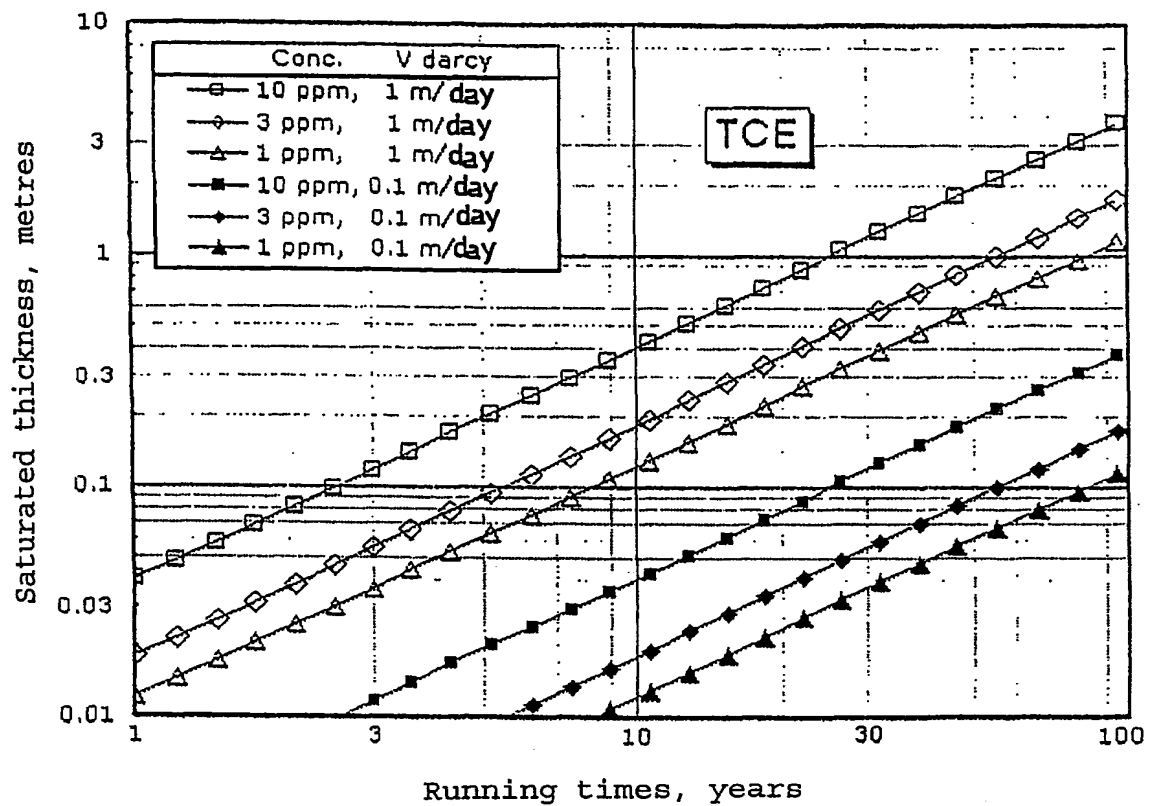## Fig.6

Concentration in the barrier after a year's running
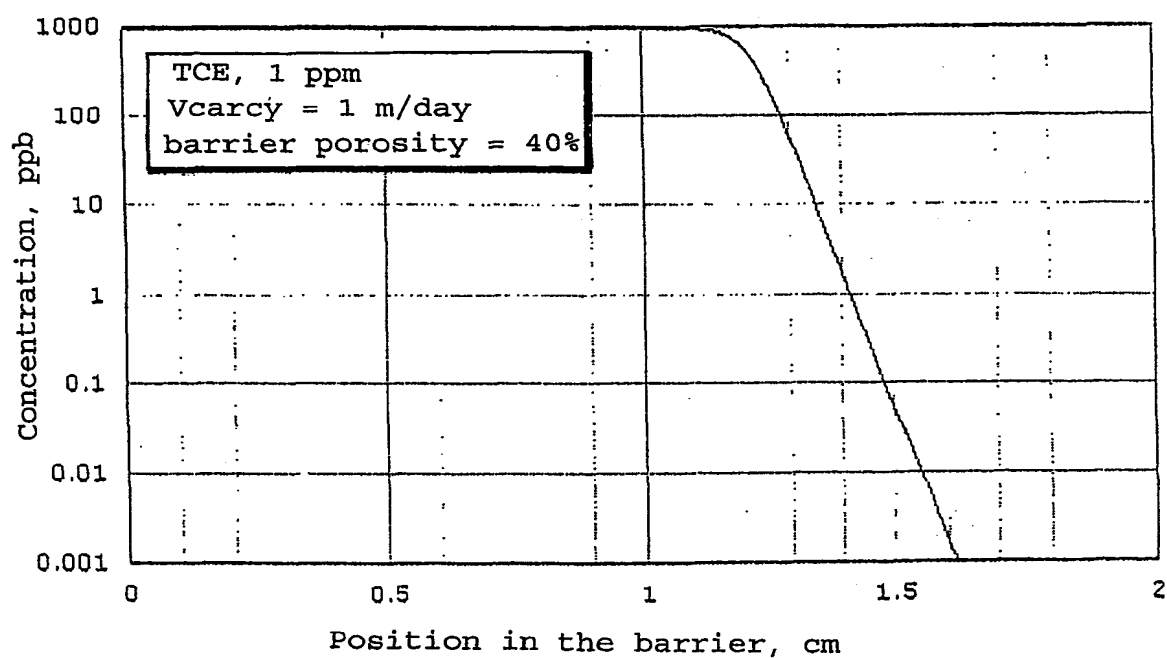
Simulation of the functioning of a zeolite barrier after a year; the groundwater moves at 1 metre/day; pollution: 1 ppm of TCE

Fig.7

Expected duration of a zeolite barrier

Advance of the saturation front with time in a zeolite bar-
rier, under various conditions of groundwater concentration
and velocity.

Fig.8

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 65826 A (ERIKSSON HAAKAN ;LARSSON KARE (SE); ORDIO AB (SE)) 23 December 1999 (1999-12-23) the whole document	1-11
X	US 5 139 682 A (MCCARTY PERRY L ET AL) 18 August 1992 (1992-08-18) the whole document	1-11
X	US 4 648 977 A (GARG DESH R ET AL) 10 March 1987 (1987-03-10) claims; example 2	1-11
X	WO 00 37364 A (ERIKSSON HAAKAN ;ORDIO AB (SE)) 29 June 2000 (2000-06-29) claims	1,3-7,9

-/--

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

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'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 October 2002	28/10/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serra, R

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 061 724 A (FLANIGEN EDITH MARIE ET AL) 6 December 1977 (1977-12-06) the whole document	1-9
A	DE 29 40 103 A (HENKEL KGAA) 14 May 1981 (1981-05-14) the whole document	1,3-7,9

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/06501

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9965826	A	23-12-1999	AU WO	4814199 A 9965826 A1	05-01-2000 23-12-1999
US 5139682	A	18-08-1992	NONE		
US 4648977	A	10-03-1987	AU AU BR CA DK EP FI JP NO	583697 B2 6704486 A 8606243 A 1262336 A1 589686 A 0228086 A2 864996 A 62183897 A 864955 A	04-05-1989 02-07-1987 29-09-1987 17-10-1989 25-07-1987 08-07-1987 01-07-1987 12-08-1987 01-07-1987
WO 0037364	A	29-06-2000	AU WO	2017800 A 0037364 A1	12-07-2000 29-06-2000
US 4061724	A	06-12-1977	NONE		
DE 2940103	A	14-05-1981	DE	2940103 A1	14-05-1981